

Claims.

1. A polymerization process, comprising:
 - polymerizing free radically (co)polymerizable monomers in the presence of a reducing agent and a polymerization medium initially comprising:
 - at least one transition metal catalyst; and
 - an atom transfer radical polymerization initiator; and
 - wherein the molar ratio of the transition metal catalyst to the atom transfer radical polymerization initiator is less than 0.5.
2. The polymerization process of claim 1, wherein the transition metal catalyst is in an oxidized state, and the polymerization process further comprises reacting the reducing agent with at least one of the transition metal catalyst in an oxidized state and a compound comprising a radically transferable atom or group to form a compound that does not participate significantly in control of the polymerization process.
3. The polymerization process of claim 1, wherein the molar ratio of the transition metal catalyst to the atom transfer radical polymerization initiator is less than 0.1.
4. The polymerization process of claim 1, wherein the molar ratio of the transition metal catalyst to the atom transfer radical polymerization initiator is less than 0.05.
5. The polymerization process of claim 1, wherein the concentration of transition metal catalyst in the polymerization medium is less than 1000 ppm.
6. The polymerization process of claim 1, wherein the concentration of transition metal catalyst in the polymerization medium is less than 100 ppm.
7. The polymerization process of claim 1, wherein the concentration of transition metal catalyst in the polymerization medium is less than 10 ppm.
8. The polymerization process of claim 1, wherein the polymerization medium further comprises a suspending medium.
9. The polymerization process of claim 1, wherein the reducing agent is an inorganic compound.
10. The polymerization process of claim 9, wherein the reducing agent is at least one of a transition metal compound, a sulfur compound of a low oxidation level, sodium hydrogen sulfite, an inorganic salt comprising a metal ion, hydrazine hydrate, and derivatives of such inorganic compounds.

11. The polymerization process of claim 10, wherein the metal ion is at least one of Sn^{2+} , Fe^{2+} , Cr^{3+} , Al^{3+} , Ti^{3+} and Ti^{4+} .
12. The polymerization process of claim 11, wherein the metal ion is at least one of Sn^{2+} , Fe^{2+} , Cr^{3+} and Ti^{3+} .
13. The polymerization process of claim 1, wherein the reducing agent is an organic compound.
14. The polymerization process of claim 13, wherein the reducing agent is at least one of alkylthiols, mercaptoethanol or carbonyl compounds that can be easily enolized, ascorbic acid, acetyl acetonate, camphosulfonic acid, hydroxy acetone, reducing sugars, monosaccarides, glucose, aldehydes, and derivates of such organic compounds.
15. The polymerization process of claim 1, wherein the atom transfer radical polymerization initiator comprises at least two radically transferable atoms or groups.
16. The polymerization process of claim 1, wherein the atom transfer radical polymerization initiator comprises a radically transferable atom or group attached to a polymer or a solid.
17. The polymerization process of claim 1, wherein the polymerization medium further comprises a solvent or suspending medium.
18. The polymerization process of claim 17, wherein the polymerization process is one of an emulsion polymerization, a mini-emulsion polymerization, microemulsion process, a reverse emulsion polymerization, and a suspension polymerization.
19. The polymerization process of claim 1, wherein the polymerization process further comprises a suspending medium, a surfactant, and a monomer phase comprising at least a portion of the radically polymerizable monomers.
20. The polymerization process of claim 19, wherein the reducing agent is capable of reacting with dissolved oxygen or react with a transitional complex that was oxidized by oxygen.
21. The polymerization process of claim 19, wherein the suspending medium is an inorganic liquid.
22. The polymerization process of claim 21, wherein the suspending medium is water.
23. The polymerization process of claim 22, wherein the reducing agent is water soluble.
24. The polymerization process of claim 1, wherein the reducing agent is at least partially soluble in the polymerization medium.

25. The polymerization process of claim 1, wherein the transition metal catalyst participates in a redox reaction between a higher oxidation state and a lower oxidation state.
26. The polymerization process of claim 25, wherein the molar ratio of reducing agent to transition metal catalyst in the higher oxidation state is 1 or less.
27. The polymerization process of claim 1, wherein the atom transfer radical polymerization initiator is at least one of an alkyl halide and a substituted ester.
28. The polymerization process of claim 19, wherein the polymerization medium further comprises a base.
29. The polymerization process of claim 1, wherein the atom transfer radical polymerization initiator comprises a radically transferable atom or group attached to a substrate.
30. The polymerization process of claim 1, wherein the reducing agent is capable of reacting with dissolved oxygen or react with a transitional complex that was oxidized by oxygen.
31. The polymerization process of claim 1, wherein the polymerization medium further comprises a base.
32. The polymerization process of claim 1, wherein the polymerization medium comprises two reducing agents.
33. The polymerization process of claim 32, wherein the rate of reduction of the two reducing agents is different.
34. The polymerization process of claim 18, wherein the atom transfer radical polymerization initiator comprises at least two radically transferable atoms or groups.
35. The polymerization process of claim 19, wherein the reducing agent is soluble in at least one of the suspending phase and the monomer phase.
36. The polymerization process of claim 1, wherein the molar ratio of reducing agent to transition metal catalyst in the higher oxidation state is more than 1.
37. The polymerization process of claim 17, wherein the polymerization medium comprises two reducing agents.
38. The polymerization process of claim 37, wherein the rate of reduction of the two reducing agents is different.
39. An emulsion or miniemulsion polymerization process, comprising:

polymerizing free radically (co)polymerizable monomers by a controlled radical polymerization process in the presence of a polymerization medium initially comprising:

- a suspending phase,
- a monomer phase; and
- a multifunctional initiator in the monomer phase.

40. The polymerization process of claim 39, further comprising adding a reducing agent and a transition metal complex to the polymerization medium.
41. The polymerization process of claim 40, wherein the reducing agent is at least one of a transition metal compound, a sulfur compound of a low oxidation level, sodium hydrogen sulfite, an inorganic salt comprising a metal ion, hydrazine hydrate, and derivatives of such inorganic compounds.
42. The polymerization process of claim 41, wherein the metal ion is at least one of Sn^{2+} , Fe^{2+} , Cr^{3+} , Al^{3+} , Ti^{3+} and Ti^{4+} .
43. The polymerization process of claim 42, wherein the metal ion is at least one of Sn^{2+} , Fe^{2+} , Cr^{3+} and Ti^{3+} .
44. The polymerization process of claim 40, wherein the reducing agent is an organic compound.
45. The polymerization process of claim 44, wherein the reducing agent is at least one of alkylthiols, mercaptoethanol or carbonyl compounds that can be easily enolized, ascorbic acid, acetyl acetonate, camphosulfonic acid, hydroxy acetone, reducing sugars, monosaccarides, glucose, aldehydes, and derivatives of such organic compounds.
46. The polymerization process of claim 40, wherein the reducing agent is added after formation of the emulsion.
47. The polymerization process of claim 39, wherein the polymerization process is one of an emulsion polymerization, a mini-emulsion polymerization, microemulsion process, a reverse emulsion polymerization, and a suspension polymerization.
48. The polymerization process of claim 39, wherein the polymerization process further comprises a surfactant.
49. The polymerization process of claim 40, wherein the reducing agent is capable of reacting with dissolved oxygen or reacting with a transitional complex that was oxidized by oxygen.
50. The polymerization process of claim 39, wherein the suspending medium is water.

51. The polymerization process of claim 50, wherein the reducing agent is water soluble.
52. A polymerization process, comprising:

polymerizing free radically (co)polymerizable monomers in the presence a polymerization medium initially comprising:

at least one transition metal catalyst; and

a atom transfer radical polymerization initiator; and

wherein the molar ratio of the transition metal catalyst to the atom transfer radical polymerization initiator is less than 0.25.

53. An atom transfer radical reaction process, comprising one of an inorganic and an organic reducing agent.

54. The atom transfer radical reaction process of claim 53, wherein the organic reducing agent is one of at least one of alkylthiols, mercaptoethanol or carbonyl compounds that can be easily enolized, ascorbic acid, acetyl acetonate, camphosulfonic acid, hydroxy acetone, reducing sugars, monosaccarides, glucose, aldehydes, and derivates of such organic compounds.

55. The atom transfer radical reaction process of claim 54, wherein the organic reducing agent is ascorbic acid or a derivative of ascorbic acid.

56. The atom transfer radical reaction process of claim 54, wherein the atom transfer radical reaction process is one of atom transfer radical addition, atom transfer radical cyclization, atom transfer coupling, and atom transfer radical polymerization.

57. The polymerization process of claim 28, wherein the base is a ligand.

58. The polymerization process of claim 31, wherein the base is a ligand.